



Thermal degradation mechanisms of wood under inert and oxidative environments using DAEM methods

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ABSTRACT

The pyrolytic behavior of wood is investigated under inert and oxidative conditions. The TGA experiment is given a temperature variation from 323 to 1173 K by setting the heating rate between 5 and 40 K/min. The results of DTG curves show that the hemicellulose shoulder peak for birch is more visible under inert atmosphere due to the higher content of reactive xylan-based hemicellulose (mannan-based for pine). When oxygen presents, thermal reactivity of biomass (especially the cellulose) is greatly enhanced due to the acceleration of mass loss in the first stage, and complex reactions occur simultaneously in the second stage when char and lignin oxidize. A new kinetic model is employed for biomass pyrolysis, namely the distributed activation energy model (DAEM). Under inert atmosphere, the distributed activation energy for the two species is found to be increased from 180 to 220 kJ/mol at the solid conversion of 10–85% with the high correlation coefficient. Under oxidative atmosphere, the distributed activation energy is about 175–235 kJ/mol at the solid conversion of 10–65% and 300–770 kJ/mol at the solid conversion of 70–95% with the low correlation coefficient (below 0.90). Comparatively, the activation energy obtained from established global kinetic model is correspondingly lower than that from DAEM under both inert and oxidative environments, giving relatively higher correlation coefficient (more than 0.96). The results imply that the DAEM is not suitable for oxidative pyrolysis of biomass (especially for the second mass loss stage in air), but it could represent the intrinsic mechanism of thermal decomposition of wood under nitrogen better than global kinetic model when it is applicable.

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1. Introduction

Bioenergy has attracted more attention than ever before globally due to its merits of being renewable, widely distributed and carbon neutral. Thermochemical processes can have highly efficient conversion of biomass to gaseous, liquid and solid products. Industrial scale implementation of these technologies requires in-depth understanding of the reaction kinetics for pyrolysis, gasification and combustion. Many studies have been reported for the thermal and kinetic behavior of biomass under inert conditions (Koufopoulos et al., 1989; Blasi, 2008) and oxidative conditions (Branca and Blasi, 2004; Safi et al., 2004; Shen et al., 2009). However direct comparisons of the characteristics under both conditions are not adequately covered, which leaves the scope for further study. The kinetic models for biomass pyrolysis (typically under inert atmosphere) can be categorized as the pseudo-mechanistic model with one or more reactions and the distributed

activation energy model (DAEM) (Capart et al., 2004; Cai and Liu, 2008) which is more accurate and recent approach (Sonobe and Worasuwannarak, 2008). The DAEM is examined in this study.

The DAEM is originally developed by Vand (1943). Since then it has been applied to analyze the complex reactions in thermal degradation of coal and activated carbon (Pitt, 1962; Solomon et al., 1988). Miura employs the DAEM for different types of coals and successfully describes a complex reaction which even has a number of parallel first-order reactions and each occurs at different rate (Miura, 1995). Later Miura improves the method to estimate the distributed activation energy ($f(E)$) and the corresponding distribution of frequency factor ($A(E)$) without the assumption of functional form of $f(E)$ and $A(E)$ (Miura and Maki, 1998). Recently, the n th-order DAEM is proposed considering the influence of temperature on the frequency factor (Cai and Liu, 2008), which gives an excellent fit to the pyrolytic mass loss curves of several types of biomass without the assumption that all reactions share the same frequency factor (A). The latest study includes the validation of the DAEM for biomass and estimation of the distributed activation energies of 62–169 kJ/mol at the conversion of 1–84% for corn stalk (Li et al., 2009). To date, there is no reported work for using

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Nomenclature

A	pre-exponential/frequency factor (1/s)
E	activation energy (J/mol)
R	Universal gas constant (8.3145 J/mol K)
t	time (s)
T	temperature (K)
V	mass of the volatiles (g)
X	solid mass (g)

Subscripts

0	initial
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1	the first stage of thermal decomposition of wood in air
2	the second stage of thermal decomposition of wood in air
∞	final or infinite
s	solid

Greek letters

α	mass fraction at time t or temperature T
β	heating rate (K/s)

the DAEM to describe the oxidative pyrolysis of biomass. This study is to fill such knowledge gap and gain better understanding of the pyrolytic characteristics of biomass. Thermo-gravimetric analysis (TGA) of two wood species is employed to have comparative evaluation of their thermal performances under both inert and oxidative environments. The experimental data at different heating rates is correlated to obtain the distribution of activation energies and coefficients corresponding to different solid conversions. The advantages and applications of this method are further estimated by comparing with the established global kinetic model in terms of the obtained activation energy and correlation coefficient.

2. Methods

2.1. Materials

The properties and the main chemical compositions of the two wood species (namely birch and pine) are shown in Table 1. The Van Soest method is employed to analyze the main components in the wood. The results show that birch consists of more hemicellulose and less lignin than pine. According to the information in the literature (Prins et al., 2006), birch and pine are categorized as deciduous and coniferous wood respectively. Wood samples in the same category have found to exhibit very similar pyrolytic behavior during the thermal conversion process (Branca and Blasi, 2004), while the differences between the thermal decomposition of these two species will be thoroughly discussed in this study.

Table 1
Properties of wood tested in the experiments.

	Pine	Birch
<i>Proximate analysis (% dry basis)</i>		
Moisture	4.16	3.82
Volatiles	79.04	83.50
Fixed carbon	16.56	12.40
Ash	0.24	0.28
<i>Ultimate analysis (% dry basis)</i>		
Carbon	50.35	49.53
Hydrogen	6.33	6.26
Nitrogen	0.17	0.19
Oxygen	38.74	39.85
Sulfur	0.01	0.07
High heating value (J/g)	20,843	20,595
<i>Constituent analysis (%)</i>		
Extractives	8.7	7.59
Hemicellulose	17.70	28.97
Cellulose	47.80	53.95
Lignin	25.50	9.43
Inorganic salts	0.30	0.06

2.2. Experimental methods

TGA experiments of solid fuel are performed by a Mettler Toledo TGA/SDTA 8951E thermo analyzer under inert (nitrogen) and oxidative (air) atmospheres. The samples are prepared by grinding large particles of solid fuel in a mortar and sieving. Tests are carried out for the particles smaller than 0.3 mm in size and less than 5 mg in mass to avoid the effect of mass and heat transfer during the process of thermal decomposition (Blasi et al., 2001) at the heating rates of 5, 10, 15, 20, 30 and 40 K/min with a temperature range from 323 to 1173 K. During the experiment the furnace of TGA is flushed with 50 ml/min nitrogen or air to maintain an inert/oxidative atmosphere during thermal decomposition of the particles.

The mass loss of the sample (TG curve) is recorded by an electronic balance against the linearly increased furnace temperature which is adjustably varied with the intensity of the applied radiative heat flux in the TG analyzer. The temperature of the crucible, regarded as the real temperature of the solid, is simultaneously measured by the thermocouples fixed on the surface of the crucible holder to obtain the SDTA curve, to determine the exothermicity or endothermicity of the pyrolytic reactions (Branca and Blasi, 2004; Fang et al., 2006). It is worth noting that the mass of crucible for holding particles is also varied during the heating process of the samples. The real mass loss of the particles (fine TG curve) is obtained by subtracting the varied mass of crucible from the crude TG curve which is directly recorded by the electronic balance under the same heating rate and atmosphere. Accordingly the mass loss rate of the samples (DTG curve) is calculated by differentiating the fine TG curve with the temperature without any smoothing correction on the data. The DTG curve without smoothing reflects the real process of thermal decomposition of wood, although it could be the cause for the divergence or non-linear performance when estimating kinetic parameter or correlating experimental data in the analytical methods (Liu, 2002; Chen, 2006).

2.3. The mathematical methods

2.3.1. The DAEM method

The distributed activation energy model (DAEM) has been employed successfully for describing coal pyrolysis (Vand, 1943; Miura, 1995; Miura and Maki, 1998). Most recent attempts are to apply this model to thermal decomposition of biomass and its components (Ferdous et al., 2002; Cai and Liu, 2008; Li et al., 2009). In this study, it is assumed that the whole thermal conversion process of wood under both inert and oxidative atmospheres is composed of a set of irreversible single (first-order) reactions occurring successively. The model is expressed as:

$$1 - \frac{V}{V_{\infty}} = \int_0^{\infty} \Phi(E, T) f(E) dE \quad (1)$$

where:

$$\Phi(E, T) = \exp\left(-\frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT\right) \quad (2)$$

and

$$V = X_0 - X; \quad V_\infty = X_0 - X_\infty \quad (3)$$

$f(E)$ is the normalized distribution curve of the activation energy, representing the variation of the activation energies of those first-order irreversible reactions. Through a numerical estimation by Miura (1995), the $\Phi(E, T)$ function varies steeply with E at a given temperature T for the heating rate β . A step function U at an activation energy E_s for $\Phi(E, T)$ is postulated to give an approximation for Eq. (2) as:

$$\Phi(E, T) = U(E - E_s) \quad (4)$$

And the Eq. (1) could be simplified to:

$$1 - \frac{V}{V_\infty} = \int_{E_s}^{\infty} f(E) dE \quad (5)$$

This condition is found to hold approximately when E_s was chosen at $\Phi(E, T) = 0.58$ for many combinations of A and $f(E)$ from the preliminary examinations, giving the expression for determining A corresponding to activation energy E :

$$\frac{0.545\beta E}{ART^2} = e^{-E/RT} \quad (6)$$

together with the following approximate equation for:

$$\Phi(E, T) \cong \exp\left(-\frac{ART^2}{\beta E} e^{-E/RT}\right) \quad (7)$$

This treatment of approximation is given mathematically at the temperature T where the i th reaction occurs for a constant heating rate β by Miura and Maki (1998):

$$\frac{d(V/V_\infty)}{dT} \cong \frac{d(V_i/V_\infty)}{dT} = \frac{A_i}{\beta} \exp(-E_i/RT)(V_{i\infty}/V_\infty - V_i/V_\infty) \quad (8)$$

It shows that the overall reaction rate could be represented approximately by the rate of the i th reaction at the temperature T while only i th reaction is occurring, where V_i and $V_{i\infty}$, respectively, are the amount of volatiles evolved and the effective volatile for the i th reaction at the temperature T . Consequently, the whole reaction system of biomass decomposition could be approximated by a set of single (first-order) reactions, occurring at different temperatures corresponding to the successive mass losses or solid conversions for a fixed heating rate.

Eq. (8) could be integrated for a constant heating rate as (Freeman, 1963):

$$1 - V_i/V_{i\infty} = \exp\left(-\frac{A_i}{\beta} \int_{T_0}^T \exp(-E_i/RT) dT\right) \cong \exp\left(-\frac{A_i RT^2}{\beta E_i} e^{-E_i/RT}\right) \quad (9)$$

The Eq. (9) could be rewritten as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) - \ln[-\ln(1 - V_i/V_{i\infty})] - \frac{E}{RT} \quad (10)$$

Since $1 - V_i/V_{i\infty} = \Phi(E, T) \cong 0.58$ was set for deriving the Eq. (6), Eq. (10) could be simplified by (Miura and Maki, 1998)

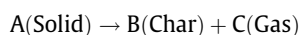
$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT} \quad (11)$$

Eq. (11) makes it easier to use the DAEM method and obtain kinetic parameters for the set of the single reactions during the thermal decomposition process of wood under both inert and oxidative

environments. For the same V/V_∞ at different heating rates (β) corresponding to the occurrence of i th reaction, Eq. (11) develops a linear relationship between (β/T^2) and $(1/T)$ with the slope of $(-E/R)$. Consequently, the activation energy E for i th reaction can be determined by the slope of the linear-fitting curve from the correlated experimental data, while the pre-exponential factor A is estimated from the intercept.

2.3.2. The global kinetic model

The global kinetic model for presenting thermal decomposition of biomass is also categorized as the separate-stage model, where the notable mass loss region is represented by a global reaction (Bilbao et al., 1997; Colomba, 1998; Fang et al., 2006; Shen et al., 2009). With regard to the notable mass loss stage(s), the global kinetic scheme for thermal decomposition of wood under inert atmosphere is described as by:



while the oxidative decomposition of wood is represented by two separate-stage reactions in reference to the work by Liu (2002) as:



The mass loss fraction α for the stage i is defined as:

$$\alpha_i = \frac{X_{i0} - X_i}{X_{i0} - X_{i\infty}} \quad (12)$$

The above pyrolytic reactions under inert and oxidative atmospheres are assumed to be governed by first-order Arrhenius Law (Zaror and Pyle, 1986; Fang et al., 2006):

$$\frac{d\alpha_i}{dt} = k_i f(\alpha_i) \quad (13)$$

where:

$$k = A \exp(-E/RT) \quad (14)$$

$$f(\alpha) = 1 - \alpha \quad (15)$$

Eq. (13) could be transformed to:

$$\frac{d\alpha}{f(\alpha)} = \frac{k}{\beta} dT \quad (16)$$

An integration function of Eq. (16) is shown as below:

$$g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT \quad (17)$$

The right integral term of Eq. (17) is approximated by Caost-Redfern method (Caots and Redfern, 1964) to be:

$$\int_{T_0}^T \exp(-E/RT) dT \approx \frac{RT^2}{E} \left[1 - \frac{2RT}{E}\right] \exp(-E/RT) \quad (18)$$

Substituting Eqs. (15) and (18) into Eq. (17), it is obtained after integration:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E} \left[1 - \frac{2RT}{E}\right]\right\} - \frac{E}{RT} \quad (19)$$

Where:

$$g(\alpha) = -\ln(1 - \alpha) \quad (20)$$

As the term of $2RT/E$ can be neglected since it is much smaller than 1, Eq. (19) could be simplified as:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (21)$$

It is well-known that the activation energy E could be obtained from the slope ($-E/R$) of Arrhenius curve ($\ln[g(\alpha)/T^2]$) against $1/T$, while the intercept of the line with y-axis is related to the pre-exponential factor A . This method is applicable to obtain the kinetic parameters for the global reaction(s), which is well-established in the literature.

3. Results and discussions

3.1. The activation energy from DAEM and global kinetic model

The inert and oxidative decomposition of wood can be described by the DAEM, while the reaction system for the overall conversion is assumed to be a set of the single reactions corresponding to the successive solid conversions. The kinetic parameters according to the degree of solid conversions under inert or oxidative atmospheres are determined by the procedures as follows (Miura and Maki, 1998):

- Measure V/V_∞ vs. T relationships at different heating rates.
- Calculate the values of (β/T^2) and $(1/T)$ at the same V/V_∞ values from V/V_∞ vs. T relationships at different heating rates.
- Plot $\ln(\beta/T^2)$ vs. $(1/T)$ at the same V/V_∞ value and determine the E (from the slope) and A (from the intercept) values from the Arrhenius plots at different V/V_∞ using the relationship in Eq. (9).

The results for birch from the above procedure are illustrated in Figs. 1 and 2. The linear and parallel development for different V/V_∞ from 0.1 to 0.85 at various heating rate in Fig. 1 indicates that the process of thermal decomposition of birch under nitrogen can be described by a set of similar single reactions (Miura and Maki, 1998). This confirms the previous result that thermal decomposition of wood under inert atmosphere is mainly determined by the degradation of cellulose. Similarly, the Arrhenius plots of birch under air are also linear and in parallel for the first stage (the selected V/V_∞ from 0.1 to 0.65) which is also dominated by the decomposition of cellulose. The development is no longer in parallel for the selected V/V_∞ from 0.7 to 0.95 in Fig. 2, reflecting a set of different chemical reactions occurring consecutively (may simultaneously) during the second stage of oxidative decomposition of wood.

The activation energy (E) and correlation coefficient (R^2) for the two species under both conditions are shown in Figs. 3 and 4. The

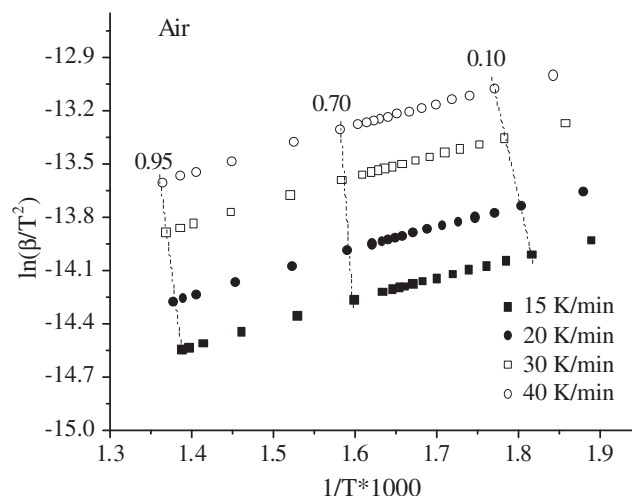


Fig. 2. Parameters from the DAEM method for birch under air at different heating rates.

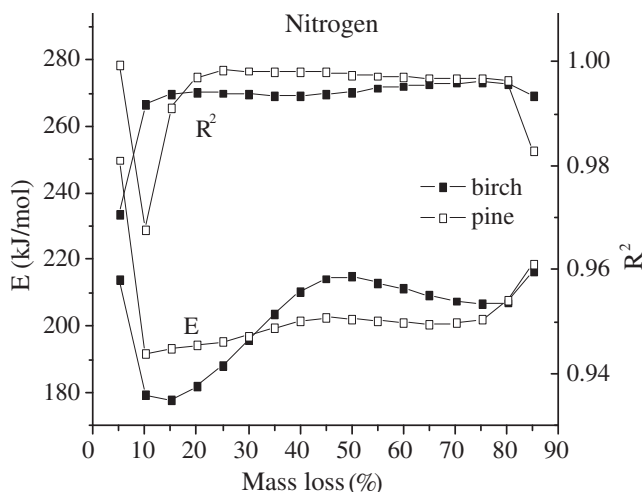


Fig. 3. The activation energy and correlation factor from the DAEM method for birch and pine under nitrogen at different mass losses.

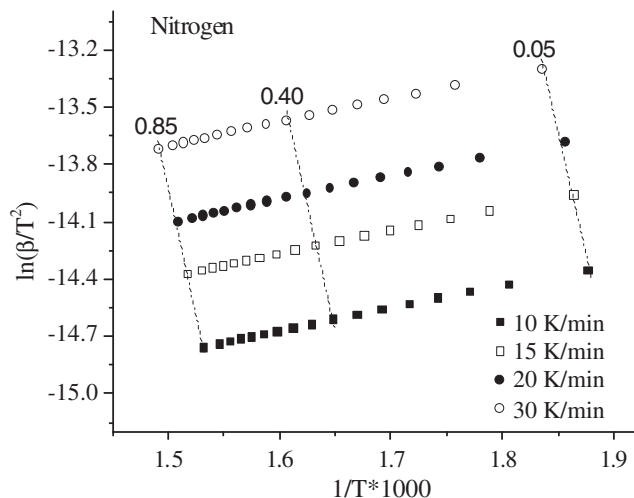


Fig. 1. Parameters from the DAEM method for birch under nitrogen at different heating rates.

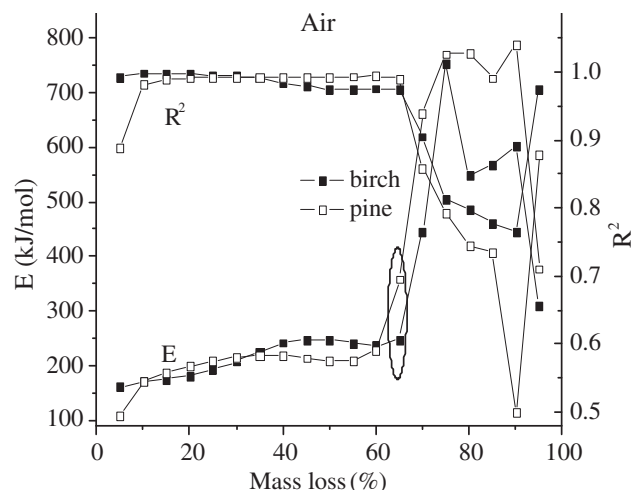


Fig. 4. The activation energy and correlation factor from the DAEM method for birch and pine under air at different mass losses.

activation energies at different mass losses (V/V_{∞}) for both species under nitrogen change slightly from 180 to 220 kJ/mol (except the case of mass loss at 5% with regard to thermal degradation of the extractives), while the correlation coefficients are all above 0.96 (Fig. 3). The values are higher than those obtained by Li et al. (62–169 kJ/mol at the conversion of 1–84% for corn stalk) (Li et al., 2009). It is plausible that the thermal decomposition of wood under inert atmosphere probably undergoes a set of single (first-order) reactions, which could be expressed by the DAEM. The activation energies vary narrowly from 175 to 235 kJ/mol corresponding to the mass loss from 10% to 60% for both species in air (Fig. 4). During the mass loss region of 70–95%, the activation energies change remarkably from 300 to 770 kJ/mol for both species. Moreover, the correlation coefficients drop below 0.9 and even reach 0.5 (Fig. 4). It is estimated that the stage corresponding to the mass loss from 70% to 100% for biomass pyrolysis under oxidative atmosphere constitutes of heterogeneous reactions (mainly char combustion), which might be enhanced by the heating rate (Sondreal et al., 2001; Fang et al., 2006; Shen et al., 2009). Since the same mass loss region in the second pyrolysis stage of wood in air is possibly not controlled by the same nominal (first-order) reaction at different heating rates, leading to the low linearity of the correlated experimental data at different heating rate.

3.2. The activation energy from global kinetic model

The activation energy (E) for the global reaction of the inert and oxidative decomposition of wood at different heating rate is shown in Table 2 and 3, together with the selected temperature region(s) corresponding to the main mass-loss stage(s). It is found that the activation energy for the two species under nitrogen varies in a narrow range between 100 and 120 kJ/mol as the heating rate increases, giving the high correlation coefficient (more than 0.96). The value for birch is a little higher than that for pine at the same heating rate, reflecting the thermal reactivity of the species under inert atmosphere. These results imply that the global kinetic scheme is reasonable to describe the inert decomposition of wood. In air, the activation energy of the first stage reaction, corresponding to the devolatilization of biomass (mainly cellulose and hemicellulose), only varies slightly (from 109 to 133 K/mol) as the heating rate increases, which is similar as the results under nitrogen. Comparatively, the substantial scatter of activation energies (from 161 to 282 K/mol) in the second stage reaction for both two species at different heating rates is possibly attributed to the modified mechanism for char oxidation. Another finding is also evident by Munir et al. (2009), observing the notable increase in value of E with a change of atmosphere from nitrogen to air.

It needs to be noted that the correlation development of experimental data is employed to obtain the activation energy for both two kinetic model (DAEM and global kinetic model). When apply-

Table 3

The kinetic parameters for pine and birch under air (global kinetic model).

Species	Heating rate (K/min)	Temperature range (°C)	E (kJ/mol)	A (s^{-1})	R^2
Birch	10	233–391	120.04	7.22×10^9	0.9857
		391–490	161.74	1.11×10^{11}	0.9698
	15	243–393	120.71	1.46×10^{10}	0.9752
		393–494.5	248.39	2.51×10^{21}	0.9768
	20	246–396	124.04	3.25×10^{10}	0.9782
		396–478	282.45	4.43×10^{20}	0.9873
	30	250–398	129.24	1.15×10^{11}	0.9796
		398–488	275.21	1.37×10^{20}	0.9926
	40	264–402	133.41	2.95×10^{11}	0.9731
		402–500	255.77	5.01×10^{18}	0.9881
	Pine	237–408	109.30	5.06×10^8	0.9842
		408–530	179.14	1.24×10^{12}	0.9823
Pine	15	244–393	121.11	1.22×10^{10}	0.9810
		393–489	225.65	1.93×10^{16}	0.9838
	20	250–400	118.67	7.59×10^9	0.9813
		400–482	254.62	2.72×10^{18}	0.9821
	30	252–402	123.61	2.74×10^{10}	0.9846
		402–504	214.94	3.87×10^{15}	0.9839
	40	260–410	121.60	1.83×10^{10}	0.9818
		410–518	201.65	3.56×10^{14}	0.9753

ing global kinetic model, the correlation coefficient (R^2), reflecting the linearity of the correlation development and also the validity of the obtained activation energy for the global reaction(s), is found to be higher than 0.96 for the two species under both inert and oxidative atmospheres. For DAEM, the value (R^2) is found to be higher than 0.96 for the set of first-order reactions at different mass losses under nitrogen, but the value is less than 0.9 for the set of reactions corresponding to the mass loss from 70% to 95% under air. From the view of apparent estimation, the global kinetic model is applicable for describing thermal decomposition of wood under both inert and oxidative atmosphere, while DAEM is not suitable for represent the wood pyrolysis in air.

However, it is obvious that the obtained activation energy and correlation coefficient for the nominal reaction(s) from the global kinetic model is substantially determined by the selection of temperature region(s) corresponding to the main mass loss stage(s) varied with the heating rate. For DAEM, the activation energies for the set of first-order reactions corresponding to the different mass losses (solid conversions) during the thermal decomposition process are not directly related to the heating rate, which are determined more objectively than that from global kinetic model. This implies that the DAEM could represent the intrinsic mechanism of wood pyrolysis better than the global kinetic model, when it is applicable.

4. Conclusions

The mechanisms of the thermal decomposition of wood are examined using DAEM methods and global kinetic model under both inert and oxidative atmosphere. The global kinetic scheme describes biomass decomposition by the nominated reaction(s) dominated in the main separated mass-loss stage(s). Because of the high correlation coefficient ($R^2 > 0.9$) extrapolated from the experimental data, the global kinetic model is estimated to be applicable for describing the thermal decomposition of wood under both inert and oxidative conditions. DAEM represents the whole reaction system of biomass decomposition by a set of first-order irreversible single reactions, giving the high activation energy than that from the global kinetic model. DAEM is found not suitable for describing the thermal decomposition of biomass under oxidative condition, because of the complexity of the second-stage decomposition reactions. It needs to be noted that DAEM

Table 2

The kinetic parameters for pine and birch under nitrogen (global kinetic model).

Species	Heating rate (K/min)	Temperature range (°C)	E (kJ/mol)	A (s^{-1})	R^2
Birch	10	261–382	118.25	3.32×10^9	0.9644
	15	260–402	117.15	2.98×10^9	0.9743
	20	270–394	120.43	6.68×10^9	0.9663
	30	280–406	122.76	1.14×10^{10}	0.9684
	40	284–408	124.03	$1.9E \times 10^{10}$	0.9694
Pine	10	270–408	120.30	3.56×10^9	0.9835
	15	272–425	114.81	1.26×10^9	0.9835
	20	270–450	101.50	9.02×10^7	0.9791
	30	278–458	103.34	1.51×10^8	0.9790
	40	278–456	103.99	2.32×10^8	0.9792

could represent the intrinsic mechanism of wood pyrolysis better than the global kinetic model, since it reflects the whole pyrolysis system in terms of consecutive solid conversion in spite of heating rate.

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